

**METHOD OF GROWING OXIDE THIN FILMS****REFERENCE TO RELATED APPLICATIONS**

The present application is a continuation of U.S. national phase application under 35 U.S.C. § 371, based on PCT/FI00/01072, filed December 4, 2000, and claims priority under 35 U.S.C. § 119 to Finnish Patent Application Number FI 19992616, filed December 3, 1999.

**BACKGROUND OF INVENTION****Field of the Invention**

The present invention relates to a method according to the preamble of Claim 1 of producing oxide films.

According to such a method a thin film containing silicon dioxide is produced on a growth substrate by an ALD method by bonding a vaporisable silicon compound onto the growth substrate and converting the bonded silicon compound to silicon dioxide.

The invention also relates to a method according to the preamble of Claim 20 of producing multicomponent oxides (i.e. mixed oxides or tertiary oxides).

**Description of the Related Art**

The continual decrease in the size of microelectronics components is leading into a situation in which  $\text{SiO}_2$  can no longer be used as the gate dielectric (gate oxide) of MOSFET (metal-oxide-semiconductor field-effect transistor) since for achieving required capacitances the  $\text{SiO}_2$  layer should be made so thin that the tunneling current increases disadvantageously high from the functional point of view of the component. To avoid the problem  $\text{SiO}_2$  has to be replaced by a dielectric material with higher dielectric constant. In that case a thicker layer of the dielectric material than  $\text{SiO}_2$  can exist. Similarly the capacitance of DRAM (Dynamic Random Access Memory) capacitors must remain nearly constant meanwhile their decrease expeditiously in size, thus the previously used  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  have to be replaced with materials having higher dielectric constants than these.

Materials having sufficiently high dielectric constants are abundant, but the problem is that the considered dielectric should be stable on the silicon surface, should most preferably be amorphous and should endure nearly unchanged under high post-treatment temperatures. Especially in the gate dielectric application a state where electrically active defects are rare

should be provided at the interface of silicon and the high permittivity metal oxide. In the memory application the structure of the capacitor dielectric must be very stable due to the applied high activation temperatures. Due to the above mentioned facts it is preferable to admix  $\text{SiO}_2$  to the metal oxide with a higher dielectric constant.

In its various forms Chemical Vapor Deposition (CVD) is the most frequently used method of producing silicon dioxide (see patent publications JP 9306906, US 4 845 054, US 4 981 724, US 5 462 899, JP 20868486, JP 6158329, JP 80061810, US 4 872 947, JP 7026383, US 5 855 957 and US 5 849 644). Mainly tetraethoxy silane (TEOS) has been used as the silicon source material, and oxygen, water, hydrogen peroxide or ozone have been used as the oxygen source material in the patent publications. In the conventional CVD the oxygen source material is always brought simultaneously with the silicon source material to the growth substrate.

The conventional CVD method is related to the difficulty of controlling the process, and neither a sufficiently good coverage with the thin layers nor a good conformality is always achieved by CVD.

The invention is based to the idea that thin films containing silicon dioxide are produced by the Atomic Layer Chemical Vapor Deposition (ALCVD) process, which is generally known also as Atomic Layer Epitaxy (ALE) or Atomic Layer Deposition (ALD).

ALD is a current method of growing thin films (US patent publication 4 085 430). According to the method a thin film is grown by means of saturable surface reactions, which are well separated from each other. The saturation is provided by means of chemisorption. In other words, the reaction temperature is selected as that the gaseous source material is stable at the growth temperature and additionally, it does not condense or decompose on the surface but is capable to react selectively with the reactive sites of the surface, e.g. with the OH groups or oxygen bridges (M-O-M) present on the oxide surface. OH groups functioning as reactive sites a so-called ligand exchange reaction takes place in which a covalent bond is formed between the surface and the source material (chemisorption). When the oxygen bridges are concerned a dissociating reaction takes place in which reaction a covalent bond is also formed (chemisorption). The bond formed by chemisorption is very strong and the surface structure formed on the surface is stable which enables the saturation of the surface by one molecular layer. The ligand exchange reactions are carried out by leading the gaseous or vaporised source

materials alternately into the reactor and by purging the reactor with an inert gas between the pulses of the source materials (T. Suntola, Thin Solid Films 215 (1992) 84; Niinisto et al. Materials Science and Engineering B 41 (1996) 23). Also even and uniform films can be grown by ALD even on large surface areas. Accordingly films can be grown on both even and heterogeneous surface as well as on a grooved surface. Controlling the thickness and the composition of the film by means of the number of reaction cycles is precise and simple.

Silicon dioxide has also been grown by the ALD process. Compounds  $\text{Si}(\text{NCO})_4$  and  $\text{N}(\text{C}_2\text{H}_5)_3$  (K. Yamaguchi et al., Appl. Surf. Sci. (1998) 130-132) have been used as source materials. Producing silicon dioxide by Molecular Layer ALE and UHV-ALE processes using  $\text{SiCl}_4$  and  $\text{H}_2\text{O}$  as source materials is also known in the literature (Surface Review and Letters, Vol. 6, Nos 3 & 4 (1999) 435 - 448).

The disadvantages of these known solutions are long reaction times, for what reason the proposed processes cannot be realized on an industrial scale.

The objective of the present invention is to eliminate the disadvantages related to the prior art and to provide a novel method, which enables a controlled growth of  $\text{SiO}_2$  containing thin films with sufficiently short reaction times.

#### SUMMARY OF INVENTION

The invention is based to the discovery that the above mentioned objectives can be achieved by using a silicon compound containing an organic ligand as the silicon source and a reactive oxygen source, such as ozone, as the oxygen source material. Multicomponent oxides in which the amount of silicon dioxide can be varied in a controlled way can easily be prepared by the proposed solution.

Furthermore, in the connection of the invention it has surprisingly been found that while growing multicomponent oxides, i.e. "tertiary oxides", by the ALD method from the corresponding source materials of silicon and some other semimetal or metal and by using suitable oxygen sources the growth rate of the multicomponent oxide is higher than that of either individual oxide. According to the invention the multicomponent oxides are therefore prepared by binding from the gas phase a suitable, vaporised silicon compound onto the growth substrate, converting the bonded silicon compound to silicon dioxide, bonding from the gas phase a vaporised metal compound or a vaporised compound of another semimetal onto the growth

substrate and converting the bonded metal compound or the compound of another semimetal to a corresponding oxide whereby the silicon compound and the compound of another semimetal and/or metal are bonded onto the growth substrate in a desired order.

More precisely, the method for preparing oxide films according to the first embodiment of the invention is characterized by what is stated in the characterizing part of claim 1.

The method of preparing multicomponent oxide films according to the invention is in turn characterized by what is stated in the characterizing part of claim 20.

Remarkable advantages are achieved with the aid of the invention. Thus, the ALD process provides a possibility for growing a multistaged interlayer containing both silicon dioxide and metal oxide prior to growing the actual metal oxide, which has a high dielectricity. The stability of the capacitor dielectric can be increased by mixing amorphous silicon dioxide into the dielectric. The preparing of multicomponent oxides and the advantages achieved thereof are described in more detail below.

It is to be noted that with the aid of the invention also pure silicon dioxide films can however be prepared. Such a silicon dioxide material can be used further in so-called STI (shallow trench isolation) structure. The function of STI is to isolate the transistors from each other in both the circuit and memory structures. At present in the lateral direction wide so-called LOCOS isolation is in use, which isolation is not suitable in the future circuits because of its bulkiness. In STI technology a horizontal narrow deep trench filled with dielectric = silicon dioxide, is etched between the circuits. Since the depth of the trench is greater than the width STI requires a method which is capable of filling the etched isolation trench conformally. By the conventional CVD method STI trenches can be filled but often the trench has to be widened in the upper part in order to avoid void formation in the middle of the STI isolation. Enlargement of the trench leads to increase of the STI area, i.e., the area of the isolation area increases. ALD is an especially suitable process for producing STI because ALD is characterized by the ability to grow silicon dioxide of uniform quality and without void formation on uneven growth substrates, especially also onto narrow trenches. Using ALD enables thus a narrower isolation area between the circuits whereby the packing density of the circuits can be increased.

In the components needed in magnetic recording silicon dioxide can be used as the isolation layer in both the writing/reading head and in the encapsulation of the writing/reading

head. In order to avoid the destruction of the magnetic properties of the layers, that are already built, the processing temperature must be low in all steps. In general, physical (sputtering) methods are used in the field, the problem of said methods being the unevenness of produced film. ALD has the capability to produce both physically and electrically homogenous thin film. It is especially preferable to use a low temperature ALD silicon dioxide process that provides a uniformly covering and electrically homogenous  $\text{SiO}_2$  thin film. In this way the reproducibility and reliability of this process step can be increased.

In the field emission displays (FED) film deposition methods producing uniform thin film on a large surface are needed. Due to the low growth temperature and the uniformity of the silicon dioxide film produced the ALD silicon dioxide process is very suitable for preparing the dielectric layer for the field emission displays.

By using especially reactive oxygen sources such as ozone, peroxide and oxygen radicals for converting the bonded silicon compound the forming temperature of silicon dioxide can be significantly decreased. According to the invention it can be operated especially at a temperature lower than 450 °C, most preferably at 400 °C at the most. In that case the whole growing cycle can also be accomplished at the same temperature, which has a great significance for industrial processing. Additionally, by using these reactive oxygen sources a very wide group of organic silicon compounds, which are not possible to be converted by e.g. water, become available.

In the following the invention is viewed more closely with the aid of a detailed description.

#### DETAILED DESCRIPTION

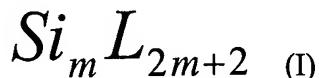
In the solution according to the invention silicon dioxide thin films and films mixed with silicon dioxide are grown in the ALD reactor preferably at the temperature of 150 - 450 °C. Even flat (such as glass or wafer) or grooved flat materials can be used as a substrate. On the surface of the substrate can also exist a so-called HSG (hemispherical grain) structure on which the film is grown. Additionally, a powdery material, which has a large surface area, can be used as a substrate. The term "growth substrate" designates in this invention the surface on which the thin film is grown. The surface can consist of the above-mentioned substrate or of a thin film grown onto the substrate or of another structure.

According to the ALD process the silicon source material is vaporised and led onto the substrate on which it reacts and forms via a ligand exchange reaction or dissociation reaction one chemisorbed molecular layer on the surface. After the reaction the reaction space is purged carefully with an inert gas to remove the unreacted source material and reaction products from the reaction space. In the connection of this invention vaporisable compounds of silicon, which contain at least one organic ligand, are used as the silicon source material. "Organic ligand" designates a hydrogen carbyl group, which is derived from an organic compound. Such a ligand has thus itself a C-C bond (e.g. an ethyl group) or it is bonded via carbon to the silicon atom or it has a C-H bond(s). According to a preferred embodiment silane, siloxane or silazane are used as vaporisable silicon compounds. These are commercially available compounds.

Especially preferably a silicon compound, which has a boiling point of 400 °C at the most at a pressure of 10 mbar is selected. Thus the ALD process can be carried out in the above-mentioned preferred temperature range of 150 - 400 °C.

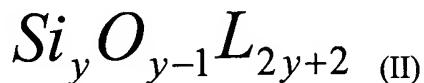
The following can be mentioned as examples of the preferred silane, siloxane and silazane compounds:

Silanes of the formula



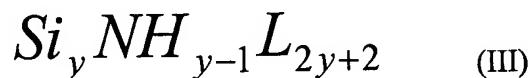
wherein m is an integer 1 - 3,

siloxanes of the formula



wherein y is an integer 2 - 4, and

silazanes of the formula



wherein y is an integer 2 - 4.

In formulae (I) - (III) each L can independently be F, Cl, Br, I, alkyl, aryl, alkoxy, vinyl (-CH = CH<sub>2</sub>), cyano (-CN), amino, silyl (H<sub>3</sub>Si-), alkylsilyl, alkoxysilyl, silylene or alkylsiloxane

whereby alkyl and alkoxy groups can be linear or branched and contain at least one substituent. Typically alkyl and alkoxy groups contain 1 -10 carbon atoms, most preferably 1 - 6 carbon atoms.

As examples of especially preferred silicon compounds amino-substituted silanes and silazanes, such as 3-aminoalkyltrialkoxy silanes, for example 3-aminopropyltriethoxy silane  $\text{NH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{-Si(O-CH}_2\text{CH}_3\text{)}_3$  (AMTES) and 3-aminopropyltrimethoxy silane  $(\text{NH}_2\text{-CH}_2\text{CH}_2\text{CH}_2\text{-Si(O-CH}_3\text{)}_3$  (AMTMS) and hexa-alkyldisilazane  $(\text{CH}_3)_3\text{Si-NH-Si(CH}_3\text{)}_3$  (HMDS) can be mentioned.

The silicon compound can also be formed during the ALD process in the connection of gas-phase reactions so that while the silicon compound is bonding, a new gas-phase silicon compound is formed which in turn is able to bond to the hydroxyl and, optionally oxide groups of the growth substrate. In this invention this phenomenon is called "in situ" formation of silicon compound. Such an in situ formed silicon compound comprises typically a silane compound, e.g. a silane compound which has a formula  $\text{SiL}_1\text{L}_2\text{L}_3\text{L}_4$ , wherein  $\text{L}_1$  represents an amino group and  $\text{L}_2 - \text{L}_4$  represent alkyl or alkoxy group. This silane compound is formed e.g. when the growth substrate is contacted with hexa-alkyldisilazane at 350 - 450 °C at the pressure of 0,1 - 50 mbar.

After bonding the silicon compound a suitable reactive oxygen source is introduced into the reaction space, said oxygen source providing the conversion of the silicon compound to silicon dioxide on the growth surface. In the following the invention is described more closely having ozone as an example. It must however be noted that instead of ozone also other oxygen source materials, listed below more precisely, can be used in many cases. Using ozone numerous advantages are however to be achieved as far as the spectrum of the silicon compounds used and the processing temperature are concerned.

Ozone, which is introduced into the reaction space, reacts with the ligands of the chemisorbed silicon source material forming OH groups and oxygen bridges on the surface. In other words ozone combusts the organic ligands and water formed in the combustion reaction forms further OH groups. After the reaction the reaction space is purged very carefully again with an inert gas to remove the unreacted ozone and the reaction products. These four steps

together form one growth cycle. The growth cycle is repeated until the film has the desired thickness.

A multicomponent film is achieved by changing the source material, i.e. by growing some other oxide onto the growth substrate between silicon dioxide growth cycles. From the point of view of the invention the growth order of the oxide compounds can be optional.

A multicomponent oxide, usually  $MsiO_x$ , is grown by vaporising the metal source material and leading the vaporised metal source material onto the substrate on which it reacts forming one molecular layer on the surface via a ligand exchange reaction and/or dissociation reaction. After the reaction the reaction space is purged carefully with an inert gas to remove the unreacted source material and the reaction products from the reaction space. After this the oxygen source material is led into the reaction space, said oxygen source material reacting with the remaining ligands (e.g. chloride ligands) of the chemisorbed metal compound complex (e.g. zirkonium complex) forming new OH groups and oxygen bridges on the surface. After the reaction the reaction space is purged again carefully. In the next step the above-described growing cycle of silicon dioxide can be carried out.

In the case of a multicomponent oxide any of the above mentioned silicon source materials can be used as the silicon compound. It must, however, be noted that also the halide compounds of silicon (silicon tetrachloride, silicon tetrafluoride, silicon tetraiodide etc.) as well as the above mentioned amino compounds are, however, suitable for being used as silicon source materials. Any of the below specified oxygen sources can be used as the oxygen source, most preferably, however, water or ozone.

One or more metals or semimetals can function as the second cation of the multicomponent oxide (i.e. tertiary oxide). Metals belonging to the groups IIIa, IVa and Va (transition metals) of the periodic table of the elements including the rare earth metals, i.e., lanthanides and lanthanoids, as well as the metals and semimetals of group IVb can especially be mentioned of the metals.

As the source material for the metal or semimetal (e.g. germanium) any stable vaporisable compound of metal in question can be used. In the example case (see example 2) the following metal source materials were used: aluminium chloride as aluminium source material, titanium tetrachloride ( $TiCl_4$ ), as titanium source material, tantalum pentachloride ( $TaCl_5$ ) as

tantalum source material, hafnium tetrachloride ( $\text{HfCl}_4$ ) as hafnium source material, zirkonium tetrachloride ( $\text{ZRCl}_4$ ) as zirkonium source material, yttrium betadiketonate ( $\text{Y}(\text{thd})_3$ ) as yttrium source material and lanthanum betadiketonate ( $\text{La}(\text{thd})_3$ ) as lanthanum source material. In the example cases water steam ( $\text{H}_2\text{O}$ ) was used as the oxygen source with aluminium, titanium, zirkonium and hafnium and tantalum source material and ozone ( $\text{O}_3$ ) was used as the oxygen source with lanthanum and yttrium source material.

Multicomponent films containing various concentrations of silicon dioxide, e.g.  $\text{SiAlO}_x$ ,  $\text{SiTiO}_x$ ,  $\text{SiTaO}_x$ ,  $\text{SiHrO}_x$ ,  $\text{SiZrO}_x$ ,  $\text{SiYO}_x$ ,  $\text{SiLaO}_x$  can be grown according to the invention by changing the number of reaction cycles of the silicon source material and ozone. In the formulae above the amount of oxide can vary and the oxide is not always completely stoichiometric.

The ratio of the amount of the metal oxide and silicon dioxide cycles can be varied. The number of cycles of the metal oxide can vary between 1 - 1000 and that of silicon dioxide between 1 - 1000. Preferably the number of cycles of the metal oxide varies between 1 - 50 and that of silicon dioxide between 1 - 50. By varying the metal oxide cycle/ silicon dioxide cycle ratio in question e.g. between 10:1 .... 1:10 the nature of the mixed oxide can be varied in a controlled way from a complete mixed oxide to a nanolaminante structure.

In growing of multicomponent oxides it has been found that the growth rate of the multicomponent oxide is higher than that of either individual oxide from which the multicomponent oxide is formed. For example the growth rate of  $\text{La}_2\text{O}_3$  from  $\text{La}(\text{thd})_3$  and ozone as well as the growth rate of  $\text{Y}_2\text{O}_3$  from  $\text{Y}(\text{thd})_3$  and ozone is  $0,2 \text{ \AA/cycle}$  which is at the same time equal to the growth rate of  $\text{SiO}_2$  from 3-aminopropylmethoxy silane and ozone. By preparing the mixed oxide of these metal oxides mentioned above with silicon dioxide using the cycle ratio of 1:1 a growth rate of more than threefold,  $0,7 \text{ \AA /cycle}$ , is achieved.

Any oxygen compound suitable for using in the ALD technology can function as the oxygen source in the above silicon dioxide and multicomponent oxide processes. Preferred oxygen source materials are for example water, oxygen and hydrogen peroxide and the aqueous solutions of hydrogen peroxide. Most preferably such oxygen sources are used which are more reactive than water towards silicon compound which contains an organic ligand. As mentioned above an especially preferred oxygen source material is ozone ( $\text{O}_3$ ). Ozone can be produced by an ozone generator and it is most preferably introduced into the reaction space with the aid of

nitrogen gas (or inert gas of same kind) whereby the concentration of ozone is about 1 - 30 vol-%, preferably about 2 - 25 vol.-%.

By using ozone as the source material organic ligands of silicon source material, said ligands forming a linear Si-C bond, can be changed at such a temperature in which the other possible ligands of the silicon source material, for example alkoxy ligands, which form a Si-O-C bond are not uncontrolled decomposing.

One or more of the following compounds can also be used as the oxygen source material:

- oxides of nitrogen, such as  $N_2O$ ,  $NO$  and  $NO_2$ ,
- oxyhalide compounds, for example chlorodioxide ( $ClO_2$ ) and perchloroacid ( $HClO_4$ ),
- peracids (-O-O-H), for example perbenzoic acid ( $C_6H_5COOOH$ ), and peracetic acid ( $CH_3COOOH$ ),
- alcohols, such as methanol ( $CH_3OH$ ) and ethanol ( $CH_3CH_2OH$ ), and
- various radicals, for example oxygen radical ( $O$ ) or hydroxyl radical ( $OH$ ).

The following non-limiting examples illustrate the invention:

### **Example 1**

$SiO_2$  films were grown in a flow type F-120 ALCVD™ reactor (ASM Microchemistry Ltd.). 3-aminopropyltriethoxy silane  $NH_2-CH_2CH_2CH_2-Si(O-CH_2CH_3)_3$  (AMTES), 3-aminopropyltrimethoxy silane  $(NH_2-CH_2CH_2CH_2-Si(O-CH_3)_3$  (AMTMS) and hexamethyldisilazane ( $CH_3)_3Si-NH-Si(CH_3)_3$  (HMDS) were used as the silicon source material. Ozone ( $O_3$ ) was used as the oxygen source material. AMTES and AMTMS were inside of the reactor. Ozone and HMDS were led into the reactor from outside. The reaction temperature of AMTES was 200 or 300 °C, that of AMTMS 300 °C and HMDS 400 °C.

The growing of  $SiO_2$  from AMTES was carried out with the aid of alternating AMTES and ozone pulses between of which the reaction space was purged carefully so that the source materials would not be simultaneously present in the reaction space. The duration of the AMTES pulse was 1,0 s and that of the purging pulse 2,0 s. The duration of the ozone pulse was 4,0 s and the duration of the purging pulse 4,0 s. The growth rate of  $SiO_2$  was 0,15 Å/reaction cycle at the reaction temperature of 300 °C and 0,28 Å/cycle at the reaction temperature of 200 °C. The refractive index of silicon dioxide grown at 300 °C was 1,4. Using AMTMS as the

source material the pulsing times were 0,5 s, 0,5 s, 2,0 s and 1,0 s, respectively, and the growth rate was 0,16 Å/reaction cycle.

The growing of  $\text{SiO}_2$  from HMDS was carried out in the same way as above. The duration of the HMDS pulse was 0,5 s and that of the purging pulse 2 s. The duration of the ozone pulse was 2,5 s and that of the purging pulse 1 s. The growth rate was 0,17 Å and the value of the refractive index varied between 1,48 - 1,57.

Based on the results, ozone can be used together with the vaporisable silicon source material for growing silicon dioxide by the ALD process. Of the silicon source materials the advantage of AMTES and AMTMS is the low reaction temperature when ozone is used as the oxygen source. This enables further the preparing of multicomponent oxides since other than metal chlorides do not stand reaction temperatures above 350 °C without decomposing.

### Example 2

Multicomponent oxides were grown in the above reactor using AMTMS as the silicon source material. In the growing processes the AMTMS pulse was 0,5 s, the purging pulse 0,5 s, the ozone pulse 3,5 s and the purging pulse 1 s. The pulse of the metal source material was correspondingly 0,5 s and the purging pulse 0,5 s. If water was used as the oxygen source the duration of the water pulse was 0,2 s and that of the purging pulse 0,5 s. Using ozone with the metal source material the duration of the ozone pulse was 3,5 s and that of the purging pulse 0,5 s. The growth rates and cycle ratios, are shown in the table below.

Multicomponent Oxide	Metal source Material	Total amount of Cycles/Cycle ratio (M:S)	Growth rate Å/cycle
SiTiOx	$\text{TiCl}_4$	1800/(1:1)	0,9
SiTaOx	$\text{TaCl}_5$	1800/(1:1)	1,1
SiHfOx	$\text{HfCl}_4$	700/(1:1)	1,23
SiZrOx	$\text{ZrCl}_4$	700/(1:1)	1,1
SiZrOx (repeat)	$\text{ZrCl}_4$	700/(1:1)	1,1
SiAlOx	$\text{Al}(\text{CH}_3)_3$	1900/(1:1)	1,0
SiLaOx	$\text{La}(\text{thd})_3$	1100/(1:1)	0,75

SiYOx	Y(thd) <sub>3</sub>	1100/(1:1)	0,73
SiYOx	Y(thd) <sub>3</sub>	2200/(2:2)	0,74
SiYOx	Y(thd) <sub>3</sub>	2200/(5:5)	0,72
SiYOx	Y(thd) <sub>3</sub>	2200/(10:10)	0,70
SiYOx	Y(thd) <sub>3</sub>	2200/(20:20)	0,64
SiYOx	Y(thd) <sub>3</sub>	2240/(40:40)	0,20

M = number of the cycles of the metal source material, S = number of the cycles of the silicon source material

The multicomponent samples were analyzed by ESCA (electron spectroscopy for chemical analysis). The thin film samples were analyzed in three different sites showing that the multicomponent oxides were very homogenous. Furthermore, the multicomponent oxides were very uniform which is typical for the ALD process when the chemistry of the growing is favorable.